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**Notes:**

1. Untranslatable words are replaced with asterisks (\*\*\*\*).
2. Texts in the figures are not translated and shown as it is.

Translated: 01:51:46 JST 05/09/2009

Dictionary: Last updated 04/14/2009 / Priority: 1. Chemistry

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**CLAIM + DETAILED DESCRIPTION**

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**[Claim(s)]**

[Claim 1]A manufacturing method of alkylene carbonate making it react in a method of manufacturing alkylene carbonate by the reaction of alkylene oxide and carbon dioxide, under at least one or more sorts of polar organic solvent existences which have an amide group or a sulfinyl group.

[Claim 2]The manufacturing method according to claim 1 whose carbon-dioxide-pressure power is more than  $60 \text{ kg/cm}^2$ .

[Claim 3]The manufacturing method according to claim 1 or 2 whose reaction temperature is not less than  $50^\circ\text{C}$ .

[Claim 4]As a polar organic solvent which it has, an amide group N, N dimethylformamide, N,N-diethylformamide, N,N-dimethylacetamide, N,N-diethylacetamide, The manufacturing method according to claim 1, 2, or 3 which uses at least one or more kinds of dimethyl sulfoxide as a polar solvent which has N-methylpyrrolidone, tetramethylurea, N,N'-dimethylethyleneurea, or a sulfinyl group.

[Claim 5]The manufacturing method according to claim 1, 2, 3, or 4 with which the amount of polar organic solvents to be used uses quantity of 2 Eq or less to 1 Eq of alkylene oxide of a raw material.

[Claim 6]The manufacturing method according to claim 1, 2, 3, 4, or 5 whose reaction pressure is below  $120 \text{ kg/cm}^2$  in more than  $60 \text{ kg/cm}^2$ .

[Claim 7]The manufacturing method according to claim 1 whose alkyleneoxide is styrene oxide and whose alkylene carbonate is styrene carbonate.

[Claim 8]The manufacturing method according to claim 1 whose alkyleneoxide is phenoxypropylene oxide and whose alkylene carbonate is phenoxy propylene carbonate.

[Claim 9]The manufacturing method according to claim 1 whose alkyleneoxide is methoxy propylene oxide and whose alkylene carbonate is methoxy propylene carbonate.

[Claim 10]The manufacturing method according to claim 1 whose alkyleneoxide is 3-phenylpropylene oxide and whose alkylene carbonate is 3-phenyl propylene carbonate.

[Claim 11]The manufacturing method according to claim 1 whose alkyleneoxide is chloropropylene oxide

and whose alkylene carbonate is chloro propylene carbonate. Halogeno one expresses fluorine, chlorine, bromine, and iodine.

[Claim 12]The manufacturing method according to claim 1 whose alkyleneoxide is 1,2-epoxy hexane and whose alkylene carbonate is 1,2-hexyl ethylene carbonate.

[Claim 13]The manufacturing method according to claim 1 whose alkyleneoxide is (R)-styrene oxide and whose alkylene carbonate is (R)-styrene carbonate.

[Claim 14]The manufacturing method according to claim 1 whose alkyleneoxide is (S)-styrene oxide and whose alkylene carbonate is (S)-styrene carbonate.

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#### [Detailed Description of the Invention]

[0001](Technical field to which an invention belongs) Without using the metal catalyst of a homogeneous system or a heterogeneous system, [ this invention ] Make the polar organic solvent which has an amide group or a sulfonyl group under supercritical carbon dioxide or subcritical carbon dioxide conditions exist, alkylene oxide is made to react, and it is related with the method of compounding carbonate efficiently.

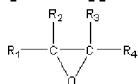
[0002](PRIOR ART) It is called for in recent years that aggravation of the earth environment by warming is becoming a serious problem, presses down use of fossil energy also internationally, and reduces the amount of carbon dioxide etc. The development research of much carbon-dioxide-fixation-ized art has been carried out as one of the methods of reducing the amount of carbon dioxide. The reaction which compounds alkylene carbonate from alkylene oxide attracts attention for many years, and many researches exist. However, the contents reported until now have that the reaction conditions which use a solid acid catalyst, an alkali-metal-salt catalyst, a homogeneous system organic metal catalyst, etc. report [ much ]. For example, a manufacturing method of the alkylene carbonate which makes a catalyst the carboxylic type cation exchange resin which uses an alkyl-group substitution ammonium cation as an opposite cation (JP,7-206846,A), A manufacturing method of alkylene carbonate using the catalyst which consists of a tungsten oxide or a molybdenum oxide (JP,7-206847,A), A manufacturing method of the alkylene carbonate which makes a catalyst the anion exchange resin which has a tertiary amine functional group or the 4th class ammonium functional group (JP,7-206848,A), There are synthesis (JP,8-53396,A) of the aryl substitution alkylene carbonate which made alkali metal salt the catalyst, a manufacturing method (U.S. Pat. No. 5,095,124) of ARUKE nil ether carbonate using a interphase move organometallic complex catalyst, etc. However, that the design of the catalyst which functions in carbon dioxide is difficult, the point that a catalyst is unstable to the moisture in the air, etc., and handling is very difficult, Problems, such as generation of a product, and that separation of a catalyst is difficult (related especially with an organometallic complex catalyst), that a catalyst is expensive and a subproduct, are produced. When using a harmful metal system catalyst especially to natural environment, there are many technical problems, such as treatment of a waste catalyst.

[0003](Object of the Invention) Although the reaction which compounds alkylene carbonate from alkylene

oxide and carbon dioxide is economical and it is a significant method also from the field of earth environment, In order to attain the industrial production aiming at environmental impact reduction, developing the new process which does not use the metal catalyst which various technical problems have accumulated is called for. In this invention, as a result of inquiring wholeheartedly that these problems should be solved, the unique function in which the polar solvent which has an amide group etc. promotes synthesis of alkylene carbonate in carbon dioxide is found out, and it came to complete this invention.

[0004](A means, i.e., this invention, for an invention to be solved) is the Norikata Arata method for carbon dioxide reacting to alkylene oxide under the polar solvent existence which has an amide group or a \*\* sulfinyl group, and manufacturing alkylene carbonate. By carrying out this invention, \*\* also made it possible to manufacture alkylene carbonate at very high efficiency, not using at all the metal catalyst needed conventionally. Hereafter, the manufacturing method of an alkylene carbonate compound by this invention is explained in detail. as the alkylene oxide used as a raw material in this invention -- a following general formula -- (1 [the-izing 1])

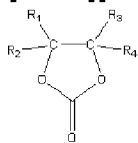
[0005][the-izing 1]



(The group from which the same group also differs may be sufficient as  $R_1$ ,  $R_2$ ,  $R_3$ , and  $R_4$ , respectively, and) [ among an upper type ] [ \*\*4\*\* ] It has hydrogen or a substituent or the aryl group of the unsubstituted carbon numbers 1-15, an alkyl group, an alkenyl group, a cycloalkyl group, and an arylated alkyl group are expressed. The substituents said here are a halogen atom, an amino group, a nitro group, a carbonyl group, a carboxyl group, an alkoxy group, an acetoxy group, a hydroxyl group, a sulfhydryl group, a sulfone group, a sulfonyl group, etc. It is alkylene oxide expressed.

[0006]If it illustrates concretely, styrene oxide, ethylene oxide, propylene oxide, Alkylene oxide, such as butylene oxide and halogeno propylene oxide, and these, Although arylated alkyl oxide, such as styrene oxide which have alicyclic oxide, such as cyclo hexyleneoxide, such as having annular oxide which has a substituent, cyclo hexyleneoxide, and a substituent, and a substituent, is mentioned, In this invention, it is not limited only to these alkylene oxide, and the three membered ring formed with two carbon atoms and one oxygen atoms will not be interfered if it is what contains at least one in the constitutional formula, and what is called epoxy compound. A reaction is presented with these one or more sorts in this invention. therefore -- the alkylene carbonate manufactured in this invention is carbonate manufactured from this alkylene oxide -- a general formula -- (2 [the-izing 2])

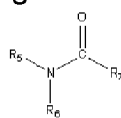
[0007][the-izing 2]



(Among a formula, the group from which the same group also differs may be sufficient as  $R_1$ ,  $R_2$ ,  $R_3$ , and  $R_4$ , respectively, and they have hydrogen or a substituent or express the alkyl group of the unsubstituted carbon numbers 1-15, an aryl group, an alkenyl group, a cycloalkyl group, and an arylated alkyl group.) The substituents said here are a halogen atom, an amino group, a nitro group, a carbonyl group, an alkoxy group, an acetoxy group, a carboxyl group, a hydroxyl group, a sulfhydryl group, sulfone, a sulfonyl group, etc. It is carbonate expressed.

[0008]If an example is illustrated, styrene carbonate, ethylene carbonate, Propylene carbonate, butylene carbonate, vinyl ethylene carbonate, chloromethyl ethylene carbonate, chloro propylene carbonate, cyclohexane carbonate, cyclopentane carbonate, styrene carbonate, etc. are illustrated.

[0009]The solvent used by this invention is an organic compound which has an amide group or a sulfinyl group, and is a general formula (3).



[0010][the-izing 3]

( $R_5$  and  $R_6$  express the alkyl group, aryl group, and cycloalkyl group which have a substituent, respectively.)

The substituents said here are a halogen atom, an alkoxy group, an acetoxy group, a carboxyl group, and an amide group.  $R_7$  is hydrogen or an alkyl group which has a substituent, respectively, an aryl group, and a cycloalkyl group, and a substituent expresses a halogen atom, an alkoxy group, an acetoxy group, a carboxyl group, and an amide group. It is an organic compound which has an amide group. General formula (4)



[0011][the-izing 4]

( $R_8$  and  $R_9$  express the alkyl group, aryl group, and cycloalkyl group which have a substituent, respectively.)

The substituents said here are a halogen atom, an alkoxy group, an acetoxy group, a carboxyl group, and an amide group. It is an organic compound which has a sulfinyl group. It may be an organic compound which comprise combination in a single molecule in [the-izing 3] and the [the-izing 4] depending on a compound.

[0012]The N, N dimethylformamide which has an amide group if an example is illustrated, Although N,N-dimethylacetamide, N,N-diethylformamide, N,N-diethylacetamide, N-methylpyrrolidone, tetramethylurea, N, and N' \*\*JIME chill ethyleneurea or the dimethyl sulfoxide which has a sulfinyl group is mentioned, In this invention, if it is a with a molecular weight of 1000 or less which consists of C, H, N, O, S and P which have an amide group or a sulfinyl group in a constitutional formula, and X (halogen) organic compound, it will not interfere. However, it is desirable that they are not that the alkylene oxide and these organic compounds of the 1 point act as solvents enough in the range below a boiling point, 2 strong-base nature, and 3 strong-acid nature. In the case of use, although it is not required, since a hydrolysis of alkylene oxide does not take

place, the direction which had removed beforehand the moisture contained in an organic compound is preferred.

[0013]The mixture solution of these organic compounds and the alkylene oxide is carried out, and it is made to react to supercritical carbon dioxide in this invention. Although the amount of addition in particular of an organic compound is not limited, it is preferred to be able to use it in 2 mol or less conveniently, to be able to use it in 0.02-1 Eq more conveniently to 1 Eq of alkylene oxide, and to use it in 0.1-0.6 Eq further most suitably.

[0014]A reaction usually advances suitably in [ temperature ] 50-300 \*\*, advances more suitably in [ temperature ] 50-200 \*\*, and advances in [ temperature ] 70-180 \*\* most suitably. Although not limited in particular, since a subproduct is usually produced above the boiling point of alkylene oxide and an organic compound, it is efficient to carry out below by a boiling point. However, when the boiling point of alkylene oxide is 50 \*\* or less, alkylene carbonate can be manufactured even if it reacts at the temperature of 0 \*\* or more. It is preferred to make it react near the boiling point of the added organic compound in that case.

[0015]Although a reaction usually advances suitably by the pressure range more than 60 kg/cm<sup>2</sup>, [ supercritical or subcritical carbon-dioxide-pressure power ] Being able to carry [ and also ] out by the pressure range of 60 kg/cm<sup>2</sup> - 120 kg/cm<sup>2</sup> more suitably, a reaction advances most suitably at the pressure range of 60 kg/cm<sup>2</sup> - 90 kg/cm<sup>2</sup>. When performing a pressure above 120 kg/cm<sup>2</sup>, since the yield of what can be manufactured becomes low, it is not desirable.

[0016]In the case of which [ of a batch type a semi batch type, and a continuation circulation type ], a reaction is carried out. Since the optimal time changes according to the kind of alkyleneoxide, reaction time cannot be limited in particular, but it is generally 5 minutes - about 48 hours suitably.

It is 5 minutes - 24 hours more suitably, and they are 30 minutes - 24 hours most suitably.

At the time of a reaction, although the reaction efficiency can be raised by agitating, it is not necessary to agitate in particular. As a result of carrying out this invention, a subproduct is not obtained at all by the generated product, but isolation refining is simply carried out by the separation generation method of the usual distillation, extraction, and recrystallization.

[0017]

[Working example]Hereafter, a work example explains this invention still in detail. However, this example explains this invention concretely and this invention is not limited only to these work examples.

[0018]After putting work-example 1 styrene-oxide 50mmol and dimethylformamide 50mmol into the reaction vessel (50mL) of the autoclave made from stainless steel and heating at 120 degrees, carbon dioxide was introduced, and it adjusted to the pressure of 78 kg/cm<sup>2</sup>, and was made to react for 15 hours. The reaction vessel was cooled after the end of a reaction, and the gas chromatograph analyzed after pressure discharge. The yield of the obtained styrene carbonate was 60%. The subproduct was not generated at all.

[0019]It reacted like the work-example 2 work example 1. However, the amount of N, N dimethylformamide was carried out as 25mmol. The yield of the obtained styrene carbonate was 53%.

[0020]It reacted like the work-example 3 work example 1. However, the amount of N, N dimethylformamide was carried out as 5mmol. The yield of the obtained styrene carbonate was 48%.

[0021]It reacted like the work-example 4 work example 1. However, reaction temperature was carried out as 160 \*\*. The yield of the obtained styrene carbonate was 85%.

[0022]It reacted like the work-example 5 work example 1. However, reaction pressure was carried out as 72 kg/cm<sup>2</sup>. The yield of the obtained styrene carbonate was 45%.

[0023]It reacted like the work-example 6 work example 1. However, reaction pressure was carried out as 87 kg/cm<sup>2</sup>. The yield of the obtained styrene carbonate was 34%.

[0024]It reacted like the work-example 7 work example 1. However, it carried out using N,N-diethylformamide 50mmol instead of N, N dimethylformamide. The yield of the obtained styrene carbonate was 35%.

[0025]It reacted like the work-example 8 work example 1. However, it carried out using N,N-diethylacetamide 50mmol instead of N, N dimethylformamide. The yield of the obtained styrene carbonate was 96%.

[0026]It reacted like the work-example 9 work example 8. However, reaction temperature was 70 \*\*. The yield of the obtained styrene carbonate was 51%.

[0027]It reacted like the work-example 10 work example 1. However, it carried out instead of N, N dimethylformamide using N-methylpyrrolidone 50mmol. The yield of the obtained styrene carbonate was 48%.

[0028]It reacted like work-example 11 work example 1. However, it carried out instead of N, N dimethylformamide using tetramethylurea 50mmol. A yield of obtained styrene carbonate was 31%.

[0029]It reacted like work-example 12 work example 1. However, it carried out instead of N, N dimethylformamide using N and N' \*\*JIME chill ethyleneurea 50mmol. A yield of obtained styrene carbonate was 36%.

[0030]It reacted like work-example 13 work example 1. However, reaction temperature was 150 \*\* and it carried out instead of N, N dimethylformamide using dimethyl sulfoxide 50mmol. A yield of obtained styrene carbonate was 57%.

[0031]Instead of work-example 14 styrene oxide, 1,2-epoxy hexane 50mmol was used and it reacted on the same conditions as a work example 1. A yield of obtained 1,2-hexyl ethylene carbonate was 54%.

[0032]Instead of work-example 15 styrene oxide, phenoxypropylene oxide 50mmol was used and it reacted on the same conditions as a work example 1. A yield of obtained hexyl carbonate was 85%.

[0033]Instead of work-example 16 styrene oxide, methoxy propylene oxide 50mmol was used and it reacted on the same conditions as the work example 1. The yield of the obtained hexyl carbonate was 36%.

[0034]Instead of work-example 17 styrene oxide, (R)-styrene oxide 50mmol was used and it reacted on the same conditions as the work example 1. The obtained styrene carbonate was R object holding a solid, and the yield was 62%.

[0035]Instead of work-example 18 styrene oxide, (S)-styrene oxide 50mmol was used and it reacted on the

same conditions as the work example 1. The obtained styrene carbonate was S object holding a solid, and the yield was 59%.

[0036] Instead of work-example 19 styrene oxide, 3-phenylpropylene oxide 50mmol was used and it reacted on the same conditions as the work example 1. The yield of obtained 3-phenyl propylene carbonate was 30%.

[0037] It reacted like the work-example 20 work example 1. However, it carried out using N,N-dimethylacetamide 50mmol instead of N, N dimethylformamide. The yield of the obtained styrene carbonate was 92%.

[0038] It reacted like the comparative example 1 work example 1. However, reaction pressure was carried out as  $52 \text{ kg/cm}^2$ . The yield of the obtained styrene carbonate was 11%.

[0039] It reacted like the comparative example 2 work example 1. However, reaction pressure was carried out as  $20 \text{ kg/cm}^2$ . The yield of the obtained styrene carbonate was 11%.

[0040] It reacted like the comparative example 3 work example 1. However, it carried out instead of the N, N dimethylformamide to be used using acetone 50mmol. Styrene carbonate was not obtained at all but the yield was 0%.

[0041] It reacted like the comparative example 4 work example 1. However, it carried out instead of the N, N dimethylformamide to be used using acetonitrile 50mmol. Styrene carbonate was not obtained at all but the yield was 0%.

[0042]

[Effect of the Invention] by this invention, it can come out and perform manufacturing alkylene carbonate, without using a metal catalyst entirely using supercritical carbon dioxide by [ which have an amide group or a sulfinyl group ] recognizing organic compound existence. In addition, in this manufacture process, since other impurities are not generated fundamentally, they can be isolated from the former of crystallization, distillation, and extraction by the simple method established technically. So, an industrial advantage -- a manufacture process can be made simple and the cost concerning a catalyst can be reduced -- is very large.

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[Translation done.]